Indian J. Phys. **73A** (3), 305–313 (1999)

IJP A
— an international journal

Theoretical study of structural phase transformation of Ta and Fe under pressure

N Singh
Department of Physics, M. D University,
Rohtak-124 001, India

Received 9 June 1998, accepted 21 September 1998

Abstract : The transition metal pair potential (TMPP) is used to predict the structural phase transitions in Ta and Fe under pressure. Ta and Fe are found to be most stable in bcc structure at observed volume V_0. At the volume 0.75 V_0 and 0.58 V_0 Ta and Fe, respectively, undergo phase transformation from bcc ⇒ fcc structure. The TMPP is also used to study phonon frequencies of these metals at observed volume. The bulk moduli and elastic constants of Ta and Fe at observed volume are calculated by including the volume contribution. The calculated values and experimental results are found to agree within 10–15%, with a few exceptions.

Keywords : Phase transformation, the transition metal pair potential (TMPP), elastic constants

PACS No. : 64.70.Kb

1. Introduction

The rapid development of high-pressure techniques has led to a renewed interest in study [1,2] of the phase transformation of the transition metals. The pressure of several megabar is needed to derive phase transformation in transition metals. For example, a solid-solid phase transformation of Mo was found [3] in a shock compression experiment at a pressure of 2.1 Mbar and a temperature of 4100 K. The lack of knowledge of elastic constants and vibrational properties of solid iron at linner core pressure (3–4 Mbar) and temperatures (4000–8000 K) have made it hard to interpret the seismological data. As a result, the study of structural phase transformation of transition metals have received a lot of attention of theoreticians [4–7], recently.

In order to interpret the results of complex structures of transition metals and rare-earths, it is still desirable to have simple methods of general applicability which are easy to

handle and can reproduce the results close to the experimental values. In the present paper, we have chosen TMPP to study the structural phase transformation of Fe and Ta, because these metals can bear high stresses at normal temperature. The phonon spectra of group-Va metals like Ta are full of anomalies [8] throughout the Brilloine zone (BZ) such as upward concavity at the origin of the [100] T and [110] T_2 branches and crossing of the [100] L and [110] L curves, so it will be interesting to study its bulk properties and phase transformation alongwith its phonon spectrum. The phase diagrams of iron at very high pressure and temperature is of considerable geophysical interest because the earths liquid outer core and solid inner core are composed primarily of this element. Thermal and compositional models of the core and the overlying mantle, which receives much of its heat from the core, are strongly dependent on our knowledge of the phase stability of iron. The phase diagram of iron is still highly uncertain at extreme pressures and the crystalline structure of inner core remains essentially unknown.

2. Theory

The total energy of a solid in second-order perturbation theory is written as

$$E = E_{eg}(n_0) + \frac{1}{2}V_{bs}(r=0) + \frac{1}{2}\sum_{i\neq 0} V_{eff}(r_i), \tag{1}$$

$E_{eg}(n_0)$ is the energy of all electrons in the solid. $n_0 = Z_s/V_0$ is the density of electrons, where V_0 is atomic volume and Z_s is the valence of the ion. The exchange-correlation corrections appropriate to electron densities in metals have been included in $E_{eg}(n_0)$. The effective ion-ion interaction $V_{eff}(r_i)$, is function of ion positions r_i. The volume dependence in this term is included through the screening function $\varepsilon(q)$, where q is the phonon wave vector. V_{bs} $(r = 0)$ can be obtained from the bandstructure part of $V_{eff}(r)$ by putting $r = 0$ and then solving the integrals following the procedure of Pettifor and Ward [9] using two-parameter Heine-Abarenkov [10] model potential and rational dielectric function [11].

Considering the non-interacting band model for s- and d-electrons, the ion-ion interaction for transition metals is written as the sum of s–s contribution, d–d repulsive and d–d attractive contributions as follows [12] :

$$V_{eff}(r) = [V_{FE}(r) + V_d(r) + V_{dd}(r)]\exp(-\pi k_B Tr/\hbar v_F). \tag{2}$$

where V_{FE} is obtained in second-order perturbation theory using the Heine-Abarenkov [10] model potential and a rational dielectric function [11]. The d-electron contributions $V_d(r)$ and $V_{dd}(r)$ are taken from the paper of Wills and Harrison (hereafter referred to be as WH) [12]. Exp $(-\pi k_B \mathrm{Tr}/\hbar v_F)$ is a damping factor obtained by Takanaka and Yamamoto [13]. Here $v_F = \hbar k_F/m$ is the Fermi velocity and k_B is the Boltzmann constant.

The bulk modulus can be obtained by differentiating eq. (1) twice and finally, we get

$$B = V\frac{\partial^2}{\partial V^2}\left[\frac{1}{2}\sum_{i\neq 0} V_{eff}(r_i)\right] + \Delta_h \tag{3}$$

The volme contribution Δ_{bs} to B arises from the volume dependence of the bandstructure part of energy $\Sigma' V_{bs}(q)$. The analytical expression of Δ_{bs} comes out to be

$$\Delta_{bs} = V\left[2\frac{\partial^2}{\partial V_0 \partial V_{osc}} + \frac{\partial^2}{\partial V_{osc}^2}\right]\sum' V_{bs}(q). \tag{4}$$

$\partial/\partial V_0$ operates on explicit volume term while $\partial/\partial V_{osc}$ operates on volume dependence of the dielectric function $\varepsilon(q)$ only.

The elastic constants for cubic crystals in longwave-length-limit $\bar{C}_{11}, \bar{C}_{12}$ and $\bar{C}_{44}$ can be obtained easily once the force constants are known. By including volume-dependent contribution Δ_{bs}, we can get the elastic moduli using the following relations :

$$C_{11} = \bar{C}_{11} + \Delta_{bs}, \tag{5a}$$

$$C_{12} = \bar{C}_{12} + \Delta_{bs}, \tag{5b}$$

$$C_{44} = \bar{C}_{44}. \tag{5c}$$

It is to be noted that C_{44} remains unaffected by volume forces because it only involves homogeneous strain at constant volume.

The effective potential defined by eq. (2) is short ranged and it is fitted to a Gaussian expansion of the form

$$v_{eff}(r) = \frac{Z_s^l e^2}{r}\sum C_i \exp(-\beta_i r), \tag{6}$$

by least square fitting method. The values of C_i and β_i obtained from this fitting, are given in Table 1. The maximum deviation in the fitted values of the effective potential at a few

Table 1. Coefficient (C_i) in Ry and exponential decays (β_i) in a.u.$^{-1}$ for the effective pair potentials.

Ta		Fe	
C_i (Ry)	β_i (a.u.$^{-1}$)	C_i (Ry)	β_i (a.u.$^{-1}$)
100966.400000	2.206391	171083.700000	2.572493
-38652.810000	1.682098	-93945.910000	2.188153
8537.997000	1.400025	35521.180000	1.567071
16530.750000	1.124783	-23514.290000	1.470403
-15162.760000	1.102442	826.818700	1.174558
13.768100	0.519244	-0.850673	0.565631
-1.235424	0.290378	-0.405779	0.44191

points upto $r = 3.7\ \pi/k_F$ is found to be 1.0 mRy for both the metals. Here k_F is Fermi-wave vector.

3. Calculations and results

There is a large overlap between electron densities of core and valence electrons in transition metals. Therefore, some of the *d*-electrons also participate in the conduction process of these metals. In this paper, the calculations for Ta and Fe are done by considering the configurations $5d^26s^2$ and $3d^64s^2$, respectively. The atomic radius r_0 at equilibrium is calculated from the observed [14] atomic volume. The *d*-electron orbital radii r_d for these metals are taken from [12]. The potential parameters D and r_c are determined by fitting the elastic constant (C_{44}) and bulk modulus (B). The values of (D, r_c) so obtained are found to be (0.47 a.u., 2.439 a.u.) and (0.70 a.u., 2.027 a.u.) for Ta and Fe, respectively.

3.1. Effective pair potential :

The effective pair potentials for Ta and Fe are given in Figures 1 and 2, respectively. The *d*-electron contribution is found to be dominant at the equilibrium position in both the metals.

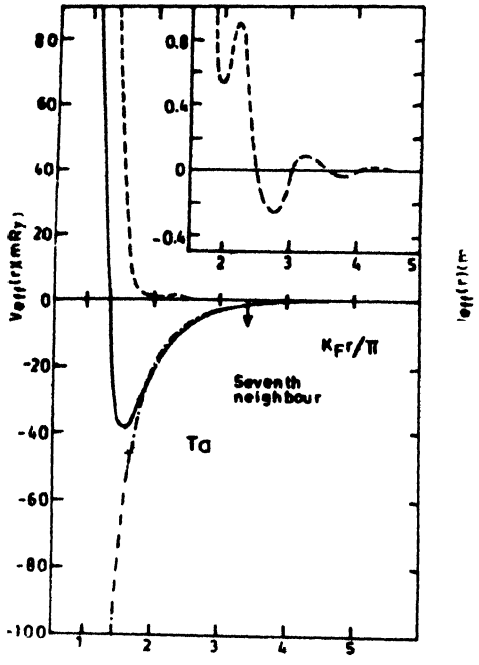

Figure 1. $V_{eff}(r)$ *vs r* for Ta. Dashed, dot-dashed and solid lines represent the contribution to $V_{eff}(r)$ due to *s*-electrons, *d*-electrons and sum of the two contributions, respectively. In the inset, the *s*-electron-contribution is shown on a magnified scale.

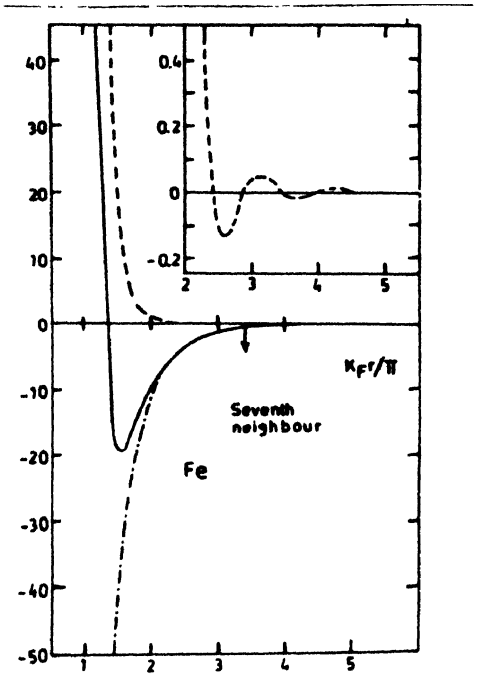

Figure 2. V_{eff} (r) *vs r* for Fe. The rest of the legend is the same as that of Figure 1.

The values of *s*- and *d*-electron contributions to $V_{eff}(r)$ at equilibrium are found to be (23.5 and –62.0 mRy) and (16.5 and –36.0 mRy) in Ta and Fe, respectively. The magnitude of oscillatory part due to *s*-electron is very small and hardly shows any structure in the total effective potential. The depth of the potential well increases and the equilibrium position of the $V_{eff}(r)$ shifted away from the centre as we go from $3d \Rightarrow 5d$ metal. $V_{eff}(r)$ decreases

faster as we move beyond equilibrium position and becomes almost negligible around seventh nearest neighbour for both the metals. Thus the contribution upto seventh shell is found sufficient to achieve convergency while computing structural properties of the metals under consideration.

3.2. Structural phase transformation :

In the present study of Ta and Fe the calculation is done for three crystal structures bcc, fcc and hcp for an ideal axial ratio c/a down to compressed atomic volume 0.55 V_0. The bandstructure energy curves as function of atomic volume are shown in Figures 3 and 4 for Ta and Fe, respectively. The bcc phase is found lowest in energy for both Ta and Fe.

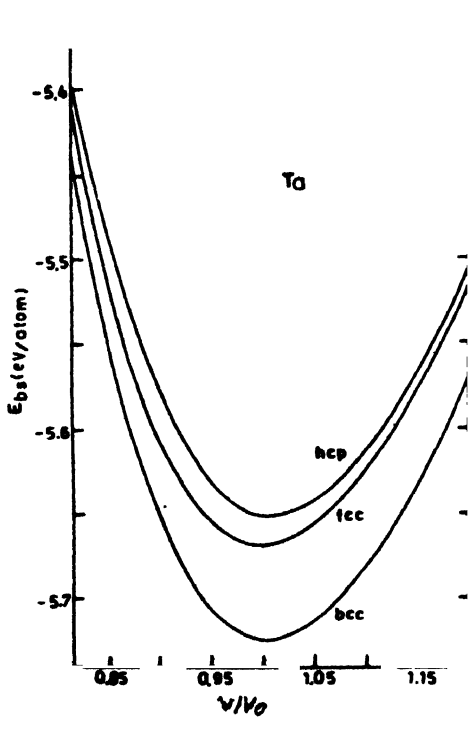

Figure 3. Band structure energy $E_{bs} = \frac{1}{2}\sum_{i\neq 0} V_{eff}(r_i)$ for fcc, bcc and hcp structures of Ta as a function of atomic volume.

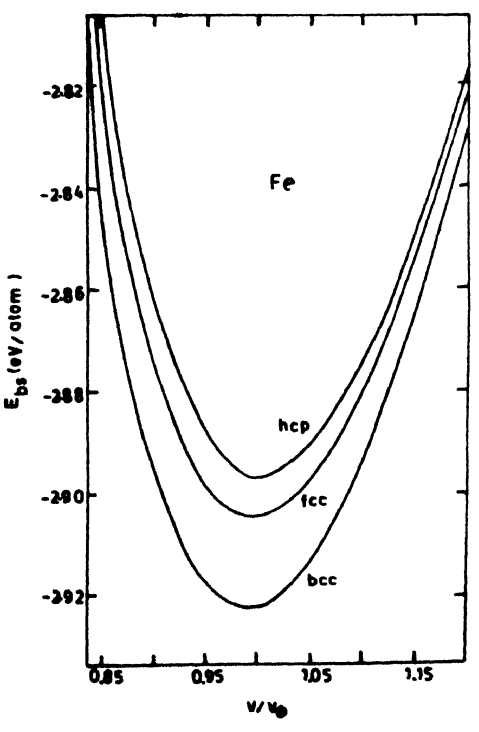

Figure 4. Band structure energy $E_{bs} = \frac{1}{2}\sum_{i\neq 0} V_{eff}(r_i)$ for fcc, bcc and hcp structures of Fe as a function of atomic volume.

The phase transition from bcc $\Rightarrow$ fcc structure takes place at the atomic volume 0.58 V_0 and 0.75 V_0 for Fe and Ta, respectively. LMTO-ASA calculations [15] in the local-spin-density approximation with gradient corrections to the exchange-correlation energy density show a phase transition from ferromagnetic α-Fe to nonmagnectic fcc phase at about 80 Kbar.

3.3. Bulk moduli, elastic constants and phonon frequencies :

The TMPP defined by eq. (2) and the effective pair potential obtained by WH are basically same. Therefore, we have compared our calculated values of elastic constants and bulk

moduli (B) with the results obtained by WH and experimental values [16] in Table 2. The theoretical values of B obtained by us in the present paper and those obtained by WH differ

Table 2. Elastic constants (C_{ij} in Mbar), Cauchy ratio (C_{12}/C_{44}), bulk modulus B (in Mbar) and volume contribution Δ_{bs} (in Mbar) of transition metals at 300 K. Values written within parentheses are difference (in percent) in theoretical values and experimental results.

		C_{11}	C_{12}	C_{44}	C_{12}/C_{44}	B
Ta	Expt. [16]	2.67	1.61	0.83	1.95	1.963
	Theor.	2.372 (–11)	1.370 (–15)	1.041 (+25)	1.31	1.704 (–13)
	Wills and Harrison [12]	2.08 (–22)	1.96 (+21)	1.51 (+82)	1.30	0.68 (–65)
	Rose and Shore [20]	3.323 (+24)	2.076 (+29)	1.038 (+25)	2.00	2.180 (+11)
	Sigalas and Papaconstantopoulos [5]	2.612 (–2)	1.702 (+6)	0.83 (0)	2.05	2.005 (+2)
	Söderlind *et al* [22]	2.91 (+10)	1.62 (0)	0.84 (0)	1.93	2.050 (+4)
	Δ_{bs}					–0.392 (–23)
Fe	Expt. [16]	2.28	1.33	1.11	1.20	1.647
	Theor.	2.341 (+3)	1.539 (+16)	1.125 (+1)	1.37	1.806 (+10)
	Wills and Harrison [12]	1.78 (–22)	1.64 (+23)	0.85 (–23)	1.93	0.496 (–70)
	Rose and Shore [20]	3.507 (+34)	2.307 (+73)	1.015 (–9)	2.27	2.719 (+65)
	Söderlind et al [21]	2.227 (–2)	1.287 (–3)	1.313 (+18)	0.98	1.600 (–3)
	Δ_{bs}					–0.414 (–38)

by about 13% in case of Ta and by 70% in case of Fe from the respective experimental values. The volume contribution Δ_{bs} to B –0.392 Mbar and –0.414 Mbar are found to be –23% and –38% for Ta and Fe, respectively. The TMPP yields overall better results for bulk moduli and elastic constants for all the metals as compared to the results obtained by WH because of the two reasons : (i) WH have completely ignored the volume contribution, which is found quite significant to bulk modulus, C_{11} and C_{12} in case of Ta and Fe. (ii) WH have employed the Thomas-Fermi dielectric function for s-electron screening. Whereas in s-electron part of TMPP it is represented by the rational dielectric function, which includes the exchange and correlation corrections through its parameters as they are obtained by fitting it with Lindhard-Taylor [17] dielectric function by least square fitting method. Overall better agreement of our calculated results with the experimental [16] values shows that the rational dielectric function combined with two-parameter Heine-Abarenkov [10] model potential is a better choice over the one-parameter Ashcroft [18] model potential and Thomas-Fermi screening function to describe the s–s interaction in TMPP. However, the s–s interaction obtained by WH is simple and has its own importance because of its originality. We have also compared our results of elastic constants with other available theoretical results [6, 19–22] in Table 2.

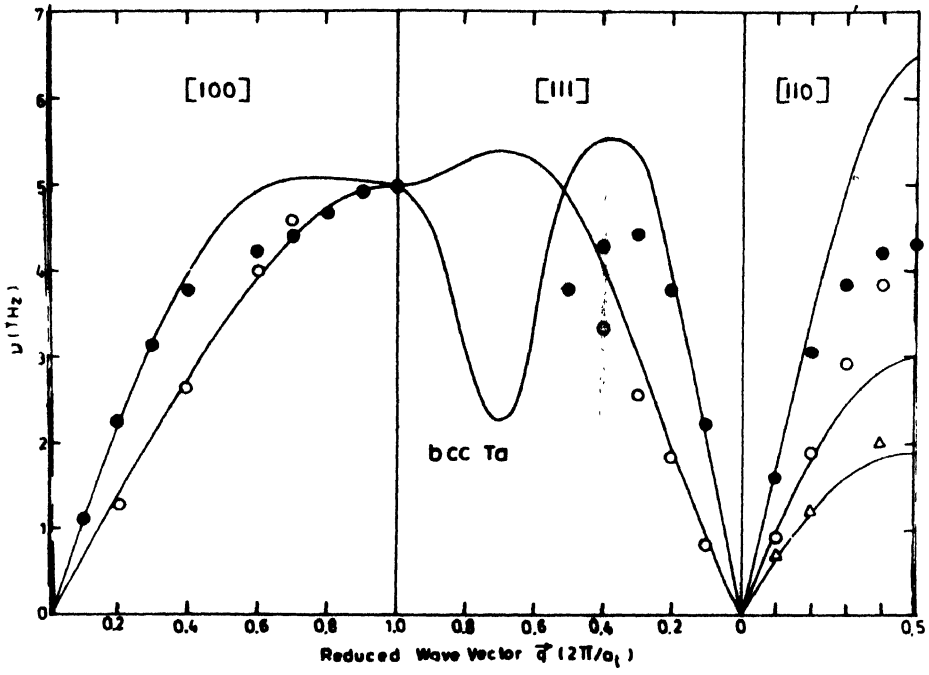

Figure 5. Phonon dispersion curves of Ta at 300 K. ●, o and Δ represent the experimental values due to Woods [23] at room temperature.

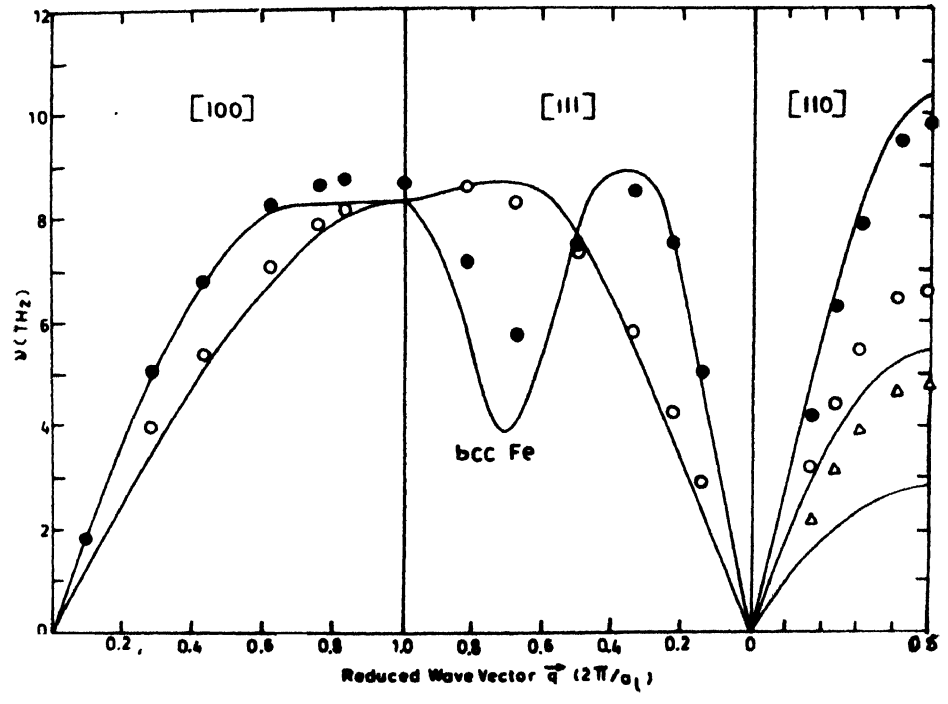

Figure 6. Phonon dispersion curves of Fe at 300 K. ●, o and Δ represent the experimental values due to Minkiewicz *et al* [24] at room temperature.

The calculated phonon spectra of Ta and Fe are shown in Figures 5 and 6. The theoretical and experimental [23,24] values of phonon frequencies agree to within 21 % for Ta and 17% for Fe, except at a few wave vectors near BZ boundary. The maximum discrepancy between calculated and experimental phonon frequencies of Ta is found to be 51% along [110] L mode at BZ boundary. Our results are found similar to those reported by Rebonato and Broughton [25] using Finnis-Sinclair [6] potential and by Animalu [26] using transition metal model potential (TMMP). Only the tight binding method [27] in the second-moment approximation, amongs the (semi) phenomenogical models known to authors, gives comparable agreement with the experimental phonon dispersion curves of Ta. It predicts incorrectly, however, the elastic constants. In order to interpret the anomalous behaviour in the phonon spectra of transition metals like Ta, the tight binding method proposed by Varma and Weber [28] may be a good choice. However, such first-principle methods are more time consuming and require much more computational efforts and cannot be easily extended to other transitition metals.

4. Conclusions

In summary, TMPP has been used to predict the structural phase transformation of transition metals Fe and Ta. The d-electron contribution has been found to decide the equilibrium position in the effective potential. The magnitude of d-electron contribution to the potential $V_{dd}(r)$ at equilibrium is found to be more than 2.5 times than the magnitude of the s-electron contribution in both the metals. The volume contribution Δ_{bs} to elastic constants C_{11} and C_{12} and bulk modulus B is found quite significant for both Ta and Fe. The calculated structural energy predicts that (i) bcc structure at equilibrium is most stable for Ta and Fe, (ii) the bcc phase transforms to fcc phase at 0.58 V_0 and 0.75 V_0 atomic volume, for Ta and Fe, respectively. Similar conclusion has been drawn by Sigalas and Papaconstantopoulos [5] for phase transformation of Ta under pressure using first principle local-density-functional theory.

Acknowledgments

The author is grateful to Prof. D G Pettifor for helping him in calculating the parameters of the rational dielectric function. The numerical calculations have been carried out with PC/AT 386 purchased out of DST grant no. SP/S2/M-39/90.

References

[1] M H Kang, R C Taylor, E J Mele and P Soven *Phys. Rev.* **B35** 5457 (1987)

[2] Y Zhou, W Lai and J Wang *Phys. Rev.* **B49** 4463 (1994)

[3] R S Hixon, D A Boness, J W Shaner and J A Moriarty *Phys. Rev. Lett.* **62** 637 (1989)

[4] Per Söderlind, R Ahuja, O Eriksson, B Johansson and J M Wills *Phys. Rev.* **B49** 9365 (1994)

[5] M M Sigalas and D A Paconstantopoulos *Phys. Rev.* **B49** 1574 (1994)

[6] M W Finnis and J E Sinclair *Phil. Mag.* **A50** 45 (1984)

[7] M S Daw and M I Baskes *Phys. Rev. Lett.* **50** 1285 (1983)

[8] A D B Woods and S H Chen *Solid State Commun.* **2** 233 (1964)

[9] D G Pettifor and M A Ward *Solid State Commun.* **49** 291 (1984)

[10] V Heine and I V Abarenkov *Phil. Mag.* **9** 451 (1964)

[11] D G Pettifor *Phys. Ser.* **T1** 26 (1982)

[12] J M Wills and W A Harrison *Phys. Rev.* **B28** 4363 (1983); **B29** 5486 (1984)

[13] K Takanaka and R Yamamoto *Phys. Stat. Sol.* **B84** 813 (1977)

[14] W B Pearson *A Handbook of a Lattice Spacings and Structure of Metals and Alloys* (New York · Pergamon) (1958)

[15] P Bagno, O Jepsen and O Gunnarson *Phys. Rev.* **B40** 1977 (1989)

[16] G Simmons and H Wang *Single Crystal Elastic Constants and Calculated Aggregate Properties* (Cambridge : MIT Press) (1971)

[17] R Taylor *J. Phys.* **F10** 1699 (1978)

[18] N W Ashcroft *Phys. Lett.* **23** 48 (1966)

[19] J Garcia-Rodeja, C Ray, L J Gallego and J A Alonso *Phys. Rev.* **B49** 8465 (1994)

[20] J H Rose and H B Shore *Phys. Rev.* **B49** 11588 (1994)

[21] Per Söderlind, R Ahuja, O Eriksson, J M Wills and B Johansson *Phys. Rev* **B50** 5918 (1994)

[22] Per Söderlind, O Eriksson, J M Wills and A M Boring *Phys. Rev.* **B48** 5844 (1993)

[23] A D B Woods *Phys. Rev* **A136** 781 (1964)

[24] V J Minkiewicz, G Sherone and R Nathans *Phys. Rev.* **162** 528 (1962)

[25] R Rebonato and J Q Broughton *Phil. Mag. Lett.* **55** 225 (1987)

[26] A O E Animalu *Phys Rev.* **B38** 3555 (1973)

[27] D Lagersie and G Allan in *Lattice Dynamics* ed. M Bal kanski (Paris . Flammarion) (1978)

[28] C M Verma and W Weber *Phys. Rev.* **B19** 6142 (1979)